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PREPARED UNDER
BUREAU OF SHIPS
DEPARTMENT OF THE NAVY
CONTRACT NO. NObs 86854

THERMOELECTRIC POWER GENERATION

A RESEARCH AND DEVELOPMENT PROGRAM ON MATERIALS AND FABRICATION TECHNIQUES

QUARTERLY REPORT NO. 3
SEPTEMBER 30, 1962

DIRECT ENERGY CONVERSION OPERATION
GENERAL ELECTRIC
950 WESTERN AVE., LYNN, MASS.

RESEARCH AND DEVELOPMENT
OF
MATERIALS AND FABRICATION TECHNIQUES
FOR
THERMOELECTRIC POWER GENERATION

JANUARY 30, 1963

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GENERAL ELECTRIC COMPANY
DIRECT ENERGY CONVERSION OPERATION
950 WESTERN AVENUE, LYNN, MASSACHUSETTS

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INTRODUCTION

This third quarterly report describes the status of the cartridge development program for the period 1 August 1962 to 30 October 1962 as funded by BuShips under Contract NObs 86854.

Section I of the report covers fabrication and test evaluation of the "cartridge couple." Section II describes the optimized cartridge configuration and predicted performance. Also included is a summary of results obtained through a generator systems study employing the optimized cartridge.

SUMMARY:

Since the last reporting period, significant advances have been made in the fabrication and testing of experimental cartridges. Life test data to 2000 hours of operation with temperature cycling has been obtained. Agreement with the predicted power level is considered excellent, but significant problems remain. Our solution to these problems along with test data will be presented in the following pages.

A study has been completed to determine the optimized cartridge configuration. Many improvements in design were made possible from experience obtained from test and fabrication problems encountered in the original design. Junction electrical resistance will be reduced by techniques to be described later in the report. It is believed that the greatest significant attainment exists in the solution to the junction problem.

SECTION I

I-1 The following is a description of cartridge fabrication and outstanding problems encountered in its assembly.

Twelve cartridges have been fabricated since August 1, 1962. The most serious and frequently re-occurring problem leading to couple failure has been oxidation in the iron-lead telluride interface due to the presence of residual flux from the soldering operation. Considerable effort has, therefore, been directed toward flux neutralization and fluxless soldering.

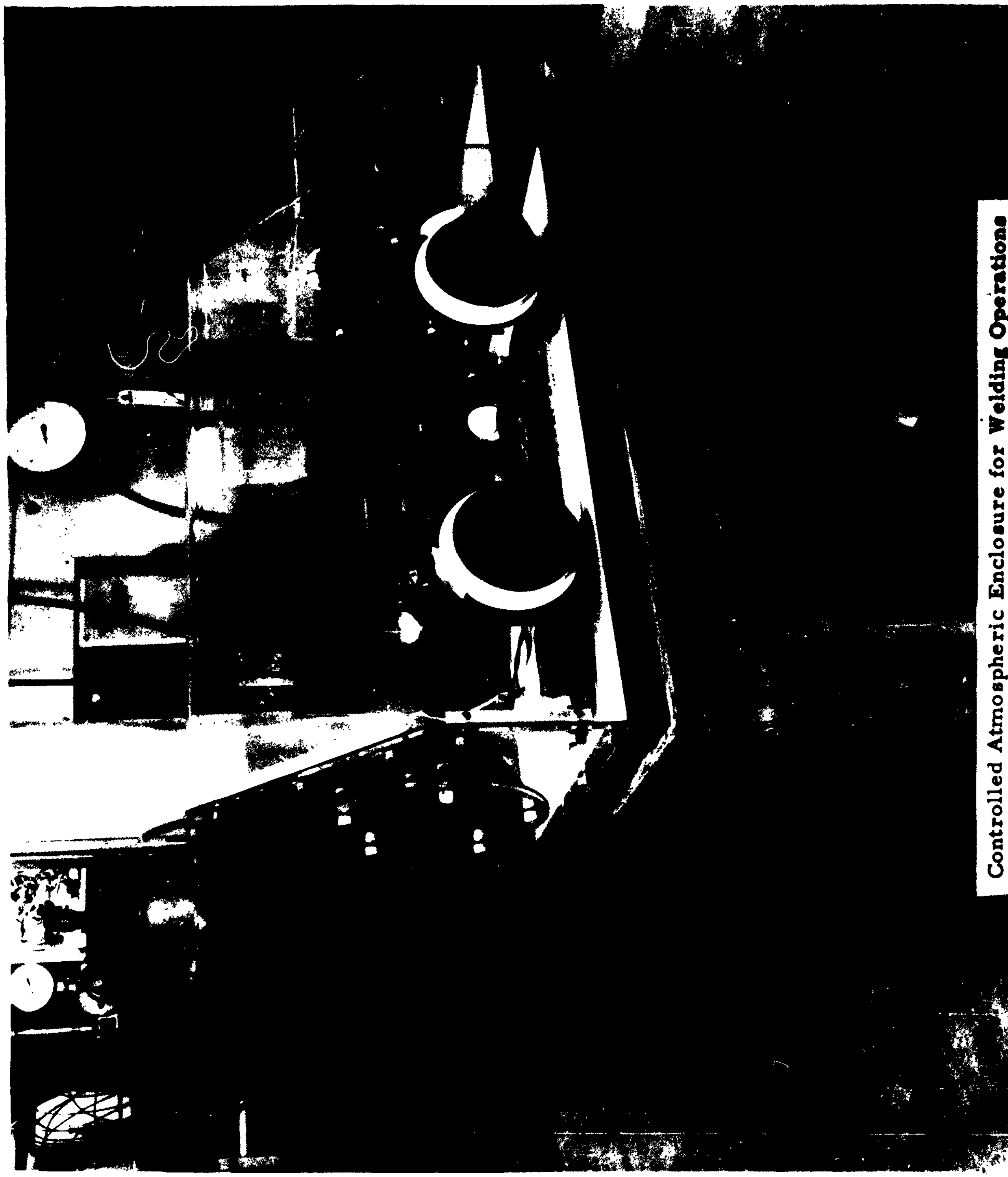
Cartridges tested to date have been soldered with procedures which require corrosive flux for the "tinning" operations. Attempts have been made to thoroughly remove the residue by using very hot water, acetone, and alcohol in the sequence stated. Parts are agitated, brushed and hot air dried between each operation.

Attempts have been made at ultrasonic tinning the 410 stainless steel terminals without flux and also the lead telluride elements. For the latter joint, the addition of argon by a specially designed gas shield, has greatly improved the ability to wet the PbTe. However, the "P" type PbTe material is very fragile and extreme care must be exercised in the technique and power level used in order to avoid cracking and crumbling of the elements.

Plans are under way to copper plate one side of the ingot iron caps, now to be brazed with tin telluride filler. This will permit tinning of the elements with a positively non-corrosive flux such as rosin and alcohol. The residue from this operation can be removed readily with solvents such as alcohol. Parts will then be fused together with the same flux, or no flux, if possible.

Brazing - Procedures have been developed to join the hot end assembly by using a fluxless filler alloy, BT Lithobraze, in a dry (-70^{o}F dewpoint) hydrogen furnace. However, a tendency to cracking persists in the Al_2O_3 material in the insulator, near the top, when copper is used as a buffer between the Kovar and the Inconel end cap. Attempts will be made with silver in an effort to reduce residual stresses caused by differential contraction during cooling. It is believed that this will be successful, since cracking has not been observed near the Kovar-Ag joint near the bottom of the assembly. Brazed assemblies will be prepared for test as soon as this problem is resolved.

Welding - The welding of casings continues, using the Inert Gas Tungsten Arc method, with the positioning fixture previously described and shown by photographs in the earlier report. A new enclosure has been procured to permit both assembly and welding operations to be performed in an argon atmosphere. The photograph (#11848) on Page 5 shows a general view of the setup.



Controlled Atmospheric Enclosure for Welding Operations

A fixture to the right of the ammeter (between glove ports) permits the application of a "pump-flush-pump" cycle to remove residual air from partially assembled cartridges that have been removed from the box after the first welding operation. The vacuum pump is shown on the bottom of the portable table. This photograph also shows the starting panel on the wall behind the box, which is coordinated with the positioner and timer, on the welding machine, to permit a fully automatic welding operation.

The quality and consistency of welding have been greatly improved by using copper heat sinks on both joining operations. The photograph (#11847) on Page 7 shows a close-up of the set-up for the first weld (base-to-sleeve) with the heat sink in place, leaving only a small part of the surface of the component exposed at the weld zone. Also shown are the elements of the split heat sink in front of the fixture tail-stock, which is used for the final welding operation. With this improved set-up the welds are made in an atmosphere of argon using a current of 9 amperes and 14 amperes respectively with a speed of rotation of 15 sec/revolution.

I-2 Work has continued on bonding iron diffusion barriers on PbTe elements for cartridge fabrication. All attempts to eliminate cracking of "p"-PbTe during the bonding cycle have been unsuccessful.

However, the cracking that occurs is such that the overall element resistance is not seriously affected, and the elements may still be used in cartridges.

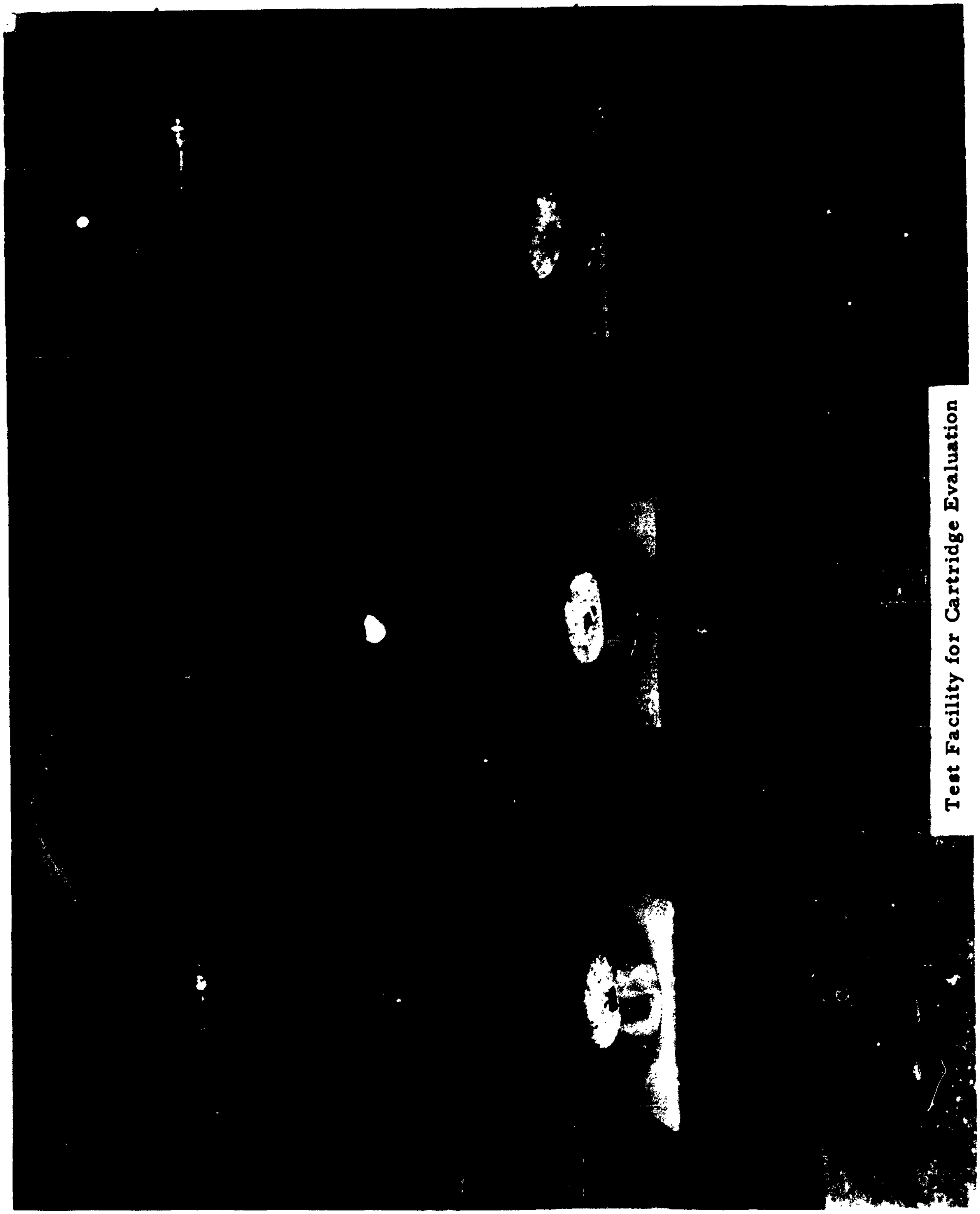
In order to try to completely eliminate our cracking problem, a program of gas pressure bonding diffusion barriers has been initiated at Battelle Memorial Institute. Several bonding experiments have been devised and assembly of material for these experiments has begun. It is hoped that the isostatic nature of the gas bonding process will produce crack-free bonded elements of higher density than now available.

In addition to gas pressure bonding techniques, brazing techniques for bonding iron diffusion barriers are being investigated. A brazing technique which looks promising has been developed by Tyco Laboratories, Inc. under BuShips Contract NObs 84770. Contact with the people at Tyco doing the brazing work has been made and their full cooperation has been promised. Retorts and gas purification systems are now being assembled to carry out their brazing procedures.

I-3 Test Equipment

The test facility shown on the next page simulates as nearly as possible actual conditions that would exist in an application of the cartridge. The flame is a mixture of natural gas (city gas) and compressed air and is controlled manually at the stand. A safety valve which will shut off the gas flow if the flame is accidentally extinguished allows continuous, unattended operation. Pressure regulators control the admission of the combustible mixture which permits close temperature control.

The heat sink, to which the cartridge is soldered, consists of two 1/8 inch by 1 inch by 1 inch copper plates with a 1/4 inch copper tube brazed to each. These are bolted to a block of insulation (Transite) which supports them and isolates them electrically from each other. See Figure 1. Tap water passed through the blocks in series results in accurate temperature establishment. Heat transfer characteristics are very good, maintaining sink temperatures at 50-70°F, depending on the seasonal temperature of the tap water. An experiment was tried where the water flow rate was reduced to the minimum that would maintain a continuous stream and the sink temperature noted above. An increase in the flow rate by a factor of 14 caused a reduction of only 5°F in sink temperature. Thus, while the sinks could be smaller, the larger area is needed for soldering electrical connections.

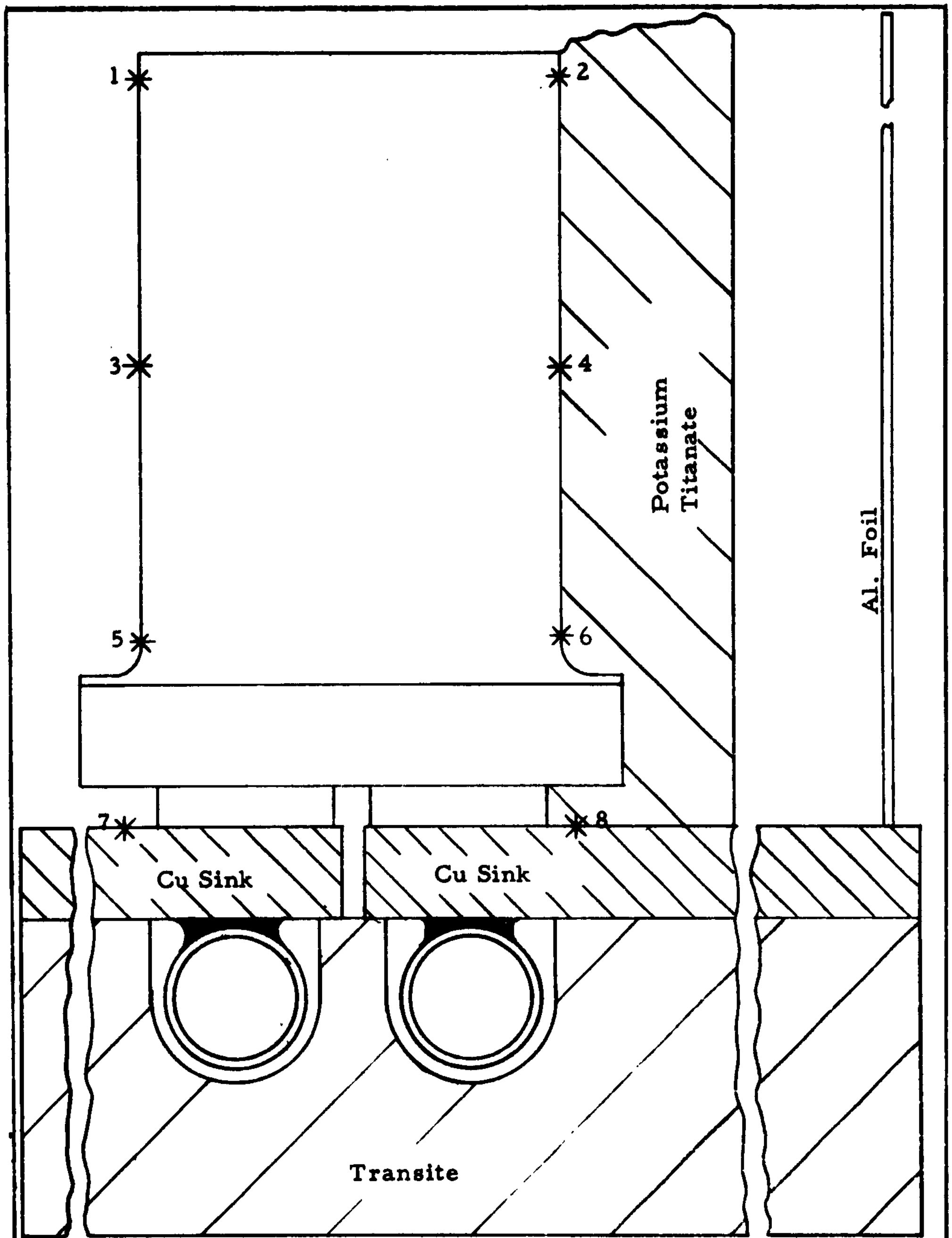


Test Facility for Cartridge Evaluation

Figure 1 shows the location of the thermocouples on the external surface of the cartridge and sink. Thermocouples 1 and 2 were used to measure hot junction temperature, while couples 3 and 6 were used to check the thermal gradient along the sleeve. Sink temperatures are monitored by couples 7 and 8 which are used in evaluating the Seebeck voltage of the cartridge.

Insulation of the cartridge was accomplished with a 3/4 inch thick band of potassium titanate and an enclosing cylinder of aluminum foil 3 inches in diameter and 3 inches high to deflect air currents. These measures simulated as nearly as possible operating conditions in "cartridge couple" applications.

In order to have standard parameters in evaluating all cartridges, it was decided to use a maximum hot junction temperature of 1150°F. Using the sink temperature it was possible to evaluate the ΔT drop through the stainless steel legs, thereby enabling us to compute a cold junction temperature of 150°F. An integrated average of the Seebeck voltage versus temperature gave a Seebeck voltage of 0.230 volts. Therefore, all power readings are taken at a matched load impedance point of 1/2 O.C.V., and is 0.115 volts for a standard comparison of cartridges.



Thermoelectric Power DECO - G.E. Co. Lynn, Mass.	FIGURE 1	Quarterly Report #3 Contract NObs 86854 R.J. Mullarkey

* Denotes location of thermocouple. Scale = 5X.

Cartridges 1 through 5 were fabricated to evaluate exploratory techniques employed in cartridge assemblies. Difficulty had been experienced in making a continuous butt weld at the hot end with 10 mil sleeve material. The weld over-lap could not be effected without burn-through. Through the use of a heat sink placed in close proximity to the weld, completion of the weld was accomplished without burn-through.

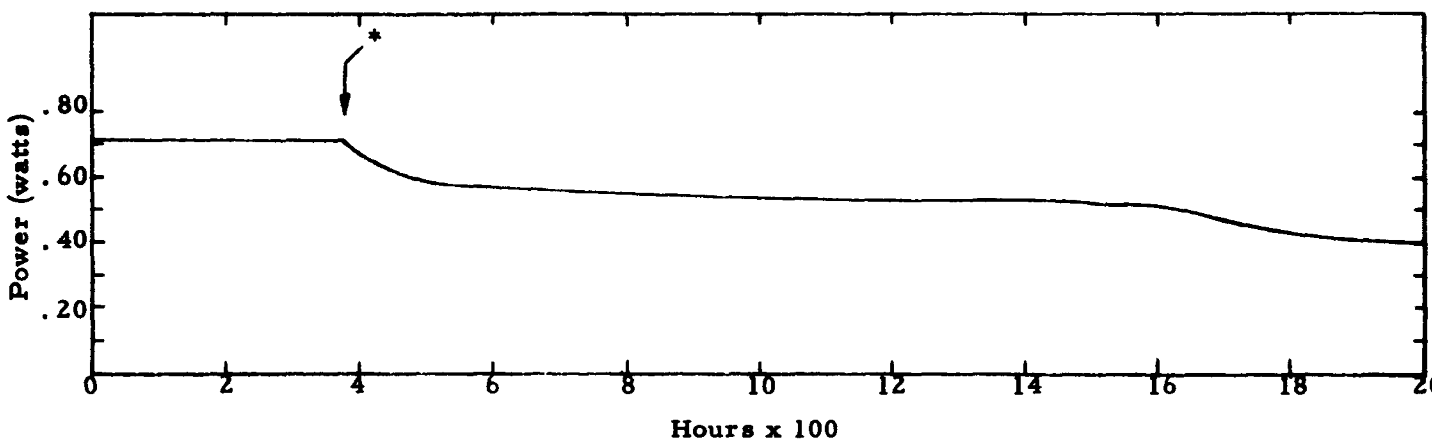
Other problems were encountered in the base soldered joint as described in an earlier section of the report. The flux problem was partially solved through the use of a neutralizing agent.

Cartridge No. 3, complete with test stand, was delivered to BuShips for their evaluation. This cartridge degraded rapidly with time but originally produced 0.65 watts with matched load. It is believed that many of the initial failures were directly attributable to the method of heat application. A propane torch with direct flame impingement on the hot end, which ordinarily is not encountered in an application, resulted in a failure in a relatively short time.

I-4 Test Results

TEC-6 originally produced 6.2 amps at 0.115 V yielding 0.71 watts of power.* After 33 hours of operation the cartridge appeared to be degrading. At the end of 210 hours of operation, power was reduced to 0.60 watts and degradation appeared to proceed at a more rapid rate. Inspection of the test set-up after 235 hours showed only point contact between the sink and cartridge, resulting in high electrical and thermal impedance. After replacement of the sink, power was recovered to 0.72 watts and remained at this level until 365 hours when the cartridge suffered an accidental overshoot in temperature of 120°F+ for 3-5 hours. From 365 hours until 1018 hours, degradation proceeded at a slow rate with a number of fluctuations finally resulting in a power output of 0.27 watts. The decision was made to remove the cartridge from the sink, disassemble and inspect it. Upon removal it was noted that the soldered connection between one stainless steel leg of the cartridge and the sink had been broken and there was only pressure contact existing here. Furthermore, there was a heavy accumulation of rust on the external surface of the base. The cartridge was cleaned and soldered to the sink again. Immediate power output was 0.54 watts, a degradation of 25% from maximum output.

* See Figure 2.



* Temperature overshoot - 120°F+ for 3-5 hours

Open circuit voltage = constant = 0.230 volts

Power values recorded at 1/2 OCV = 0.115 volts

Thermoelectric Power DECO - G.E. Co. Lynn, Mass	TEC-6 FIGURE 2	Quarterly Report #3 Contract NObs 86854 R.J. Mullarkey

Since loss of power had appeared gradually and over a long period of time (1% per 10 hours), it was believed erroneously that degradation of the cartridge had taken place rather than degradation of the sink-cartridge soldered joint.

It was decided to leave the cartridge in operation in order to acquire more data from it. At 1500 hours, the power output was 0.52 watts, a further degradation of 3% over the past 500 hours. The rate of degradation continued to increase, and at 1640 hours the power output was 0.50 watts. Further degradation continued until at 1686 hours the power output was 0.40 watts. The power remained constant at this level to 2000 hours, at which time the cartridge was removed from the test stand for sectioning and inspection. During this 2000 hour operating period, the cartridge had undergone 50 thermal cycles, the first one occurring after 169 hours of operation. A thermal cycle consists of flame extinguishment while the sink remains in operation, causing the temperature of the cartridge to be reduced to less than 100°F within 5 minutes, whereupon the flame is ignited again.

TEC-7 initially produced a power output of 0.20 watts and gradually increased to 0.62 watts after 47 hours of operation. After 148 hours, the power had decreased to 0.55 watts when the flame for the heat source was extinguished because of mechanical difficulties in the air and gas lines. When ignited again, the power was 0.45 watts and gradually increased to 0.52 watts at 163 hours. Power started dropping again, and at 167 hours the current had decreased to nearly zero.

Disassembly and inspection of the cartridge showed that a silver shim used to compensate for a difference in element height at the hot junction had shifted during assembly leaving only point contact between the leg and the bridge between legs. This shift was sufficient to allow an open circuit voltage reading but lowered current carrying capacity.

The increase in pressure at operating temperature caused the silver to warp slightly, decreasing contact resistance. Evidently the thermal cycle caused the shim to shift and break contact completely. Several turns of sheet mica were wrapped around the elements to isolate them electrically from the Inconel sleeve. The silicon resin binder in the mica carbonized in the region above 1000°F so that it acted as a bridge between the legs. Although Seebeck voltage could be measured, current carrying capacity was low due to the point contact of this section.

TEC-8 had an original power output of 0.89 watts which degraded to 0.76 watts after 75 hours. The first thermal cycle occurred at this time, and power after cycling was only 0.71 watts. There was a further degradation to 0.59 watts at 94 hours when another cycle occurred. Power after this cycle was only 0.57 watts, and it was necessary to increase flame temperature slightly to maintain design O.C.V. of 0.230 volts. Returning to the previous temperature showed a decrease in Seebeck voltage with time until, at 152 hours, it was 0.200 volts (O.C.V.) with a power output of 0.26 watts.

At this time the cartridge-to-sink joint was examined and found to be inadequate. After resoldering to the sink, voltage was zero. Consequent disassembly of the cartridge showed a short circuit caused by a bridge of solder at the cold junction resulting in final failure.

Examination of the components showed the 5 mil silver buffer between the end cap and the hot-side insulation to be divided into a "dull" circle plus a "shiny" ring 40 mils wide surrounding it. Under microscopic inspection, the shiny surface was composed of a large grain structure with a definite crack at the boundary between the two grain structures. The ability to see the large grains was due to thermal etching occurring during operation of the cartridge. Since the hot-side insulation has a smaller diameter than the silver buffer, the buffer "grew" in the region where it was unsupported.

On each iron end cap at the cold junction, there was a band of rust caused by the corrosive flux used in soldering. Washing the element-base assembly after soldering reduces the formation of rust but due to the porosity of the iron end caps does not eliminate all of the flux that causes corrosion. Further investigation of fluxless soldering is continuing.

The bridge at the hot junction was a 35 mil silver disc. Upon disassembly it was found that sublimation had occurred from areas that were not in contact with other components, i.e., around the circumference and the 50 mil gap over the split between elements. In these areas a whisker growth appeared to exist.

Further investigation is being pursued at this time to determine why the silver sublimed, reasons for the whisker growth and why this was the only cartridge to suffer adverse effects after thermal cycling.

TEC-9 failed to register voltage on test. Internal inspection showed a bridge of solder causing a short circuit at the cold junction. This appeared to be caused by over-heating of the cold junction while soldering the cartridge to the sink.

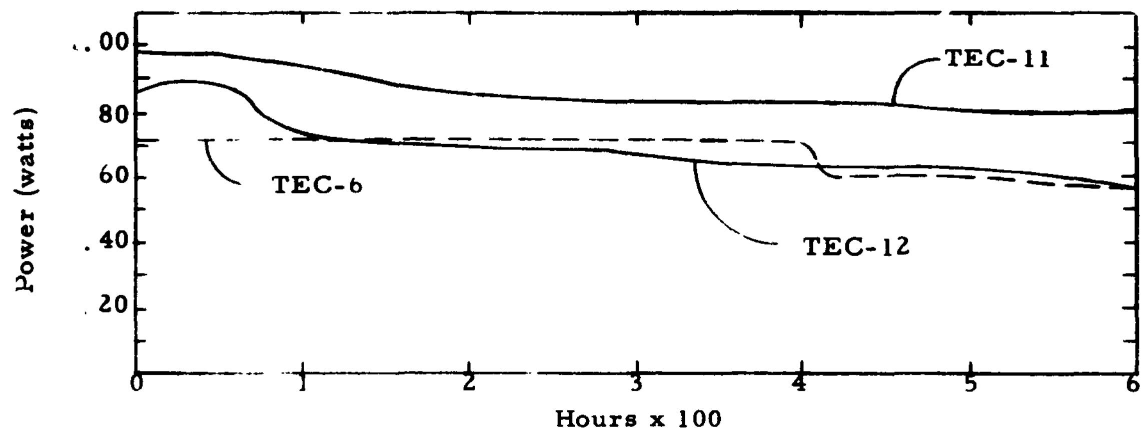
TEC-10 produced no voltage for the first 20 minutes of operation. Operating conditions then appeared to "seat" the stack-up, and TEC-10 began to produce power which reached a maximum of 0.51 watts after 24 hours. It degraded to 0.29 watts at 142 hours and remained fairly constant at this power until 189 hours when degradation proceeded at a more rapid rate. TEC-10 produced the same effect as TEC-8 where Seebeck voltage started dropping at 281 hours. At 330 hours, O.C.V. was 0.210 volts and power output was 0.12 watts.

At this time TEC-10 had been removed from its sink but has not been disassembled. Inspection will be made shortly to determine: 1) the inability to produce power until run for 20 minutes (believed due to a mismatch of components during assembly), 2) did this cause an uneven heat flux through the elements resulting in lowered Seebeck voltage, and 3) if the 35 mil silver shim sublimed as it did in TEC-8.

The major difference in these 5 cartridges was in the silver bridge at the hot junction. TEC 6 and 7 had two 5 mil circular shims with a semi-circular shim to compensate for difference in element height. The elements in TEC-8, 9 and 10 were polished so that no compensating shim was required and a 35 mil disc of silver was used as the bridge.

The purpose of the thicker shim was to increase plastic flow for better seating of the components and the reduction of internal resistance by eliminating some of the contact resistance in the circuit. Due to the sublimation of this heavier disc (not noticed in the thinner shims) and the drop-off of Seebeck voltage (unnoticed in the other cartridges), it was decided to revert to the former assembly when fabricating TEC-11 and also to change the axial compression load used during welding from 12 lbs. to 25 lbs.

TEC-11 had an initial power output of 0.115 volts x 8.60 A = 0.99 watts. After 96 hours of operation the power was 0.96 watts and degraded further to 0.90 watts at 143 hours (see Figure 3). Between 143 hours and 150 hours the cartridge experienced two thermal cycles, each of which caused a further degradation (power at 150 hours = 0.86 watts). This is the first instance of cycling causing a noticeable degradation of a cartridge. Since end cap temperature and Seebeck voltage remained the same, there was increased resistance in the circuit due to cracking of the elements or the extension of an existing crack. However, over the next 450 hours and 6 more cycles, the degradation was slight (5%). At 600 hours, power was 0.81 watts, 82% of the initial power. TEC-11 will remain on test fur further evaluation.



Comparison of TEC-6, TEC-11, TEC-12 over a 600 hour period.

Open circuit voltage = constant = 0.230 volts

Power values recorded at 1/2 OCV = 0.115 volts

Thermoelectric Power DECO - G.E. Co. Lynn, Mass.	FIGURE 3	Quarterly Report #3 Contract NObs 86854 R. J. Mullarkey

TEC-12 was the first cartridge to incorporate a brazed assembly on the hot side (silver shim, alumina-Kovar insulator and end cap brazed together before assembly) which is designed to minimize thermal resistance. Utilizing a brazed assembly at this time was mainly to check the feasibility of manufacturing techniques and not to measure efficiency.

The "p" leg used in TEC-12 was severely cracked and had almost twice the electrical resistance of the "p" leg in TEC-11.

TEC-12 had an initial power output of 0.86 watts which increased to 0.89 watts after 17 hours (see Figure 3). The cartridge degraded rapidly to 0.72 watts at 117 hours. Further degradation proceeded at a fairly constant but much less rapid rate through five more thermal cycles and 500 hours until the power was 0.58 watts at 600 hours. TEC-12 will also remain on test for further evaluation.

I-5 Conclusions

Thermal cycling appears to have no appreciable effect on the cartridge. Two of the nine (9) cycles experienced by TEC-11 were exceptions to this as noted; however, the degradation of TEC-6 was not attributed to any of the 50 cycles it underwent.

Seven minutes after ignition (allowing time for stabilization of the thermal gradient), power output would be equivalent to the preceding cycle.

Keeping the cartridge on load for extended periods of time (up to 16 hours) had no effect other than the Peltier Effect. The sleeve thermocouples near the end cap registered a temperature drop up to 40°F and a corresponding drop in voltage from 1/2 O.C.V. = 0.115 V to 0.110 V due to the decreased ΔT along the elements. Within two minutes after removal of the load, the O.C.V. and temperature would return to normal. (All power readings in this report were taken immediately after application of the load to minimize errors caused by the Peltier Effect.)

I-6 Future Testing

Further testing of the present cartridge will continue until the optimized cartridge is ready for evaluation. Testing of the optimized cartridge will be conducted along similar lines; however, an extensive investigation of components will also be included.

Problems have been encountered with the solder joint between sink and cartridge. This has led to incorrect data when the sink separates gradually from the cartridge (gradual degradation of the joint was first attributed to the cartridge in the case of TEC-6). Accidental over-heating of the cartridge while soldering it to the sink has caused the solder between the legs and base to flow and short circuit the cartridge. A number of designs are being developed that will hold the cartridge to the sink mechanically and/or change the position of the solder joint (such as putting copper inserts in the stainless steel base) to overcome the previously mentioned problems.

A fixture to hold the sleeve to the base has been devised which will allow non-destructive disassembly of the cartridge for inspection. While this is suitable for test purposes, the welded sleeve to base configuration will be retained in future assemblies.

I-7 Cartridge Evaluation by General Engineering Laboratory, Schenectady, New York

One of the early thermoelectric cartridges (TEC-4) was delivered to the General Engineering Laboratory for their evaluation. This effort was conducted by R. Thompson at the Laboratory and the results are included in their entirety.

Test of DECO Thermoelectric Cartridge

An early prototype TE cartridge fabricated by DECO was supplied to GEL for testing. This unit had been operated at DECO and reportedly developed an open circuit voltage of 0.22 V and a power at 1/2 open circuit voltage of 0.65 watts*. Temperatures in this preliminary test were unknown.

During a light abrasive cleaning of the hot cap surface, it was noted that a ceramic patch over a weld blowout was not visible. Re-sealing of the cartridge by welding was readily accomplished. An aluminum chill block was used to minimize possible heat damage to the elements or junctions.

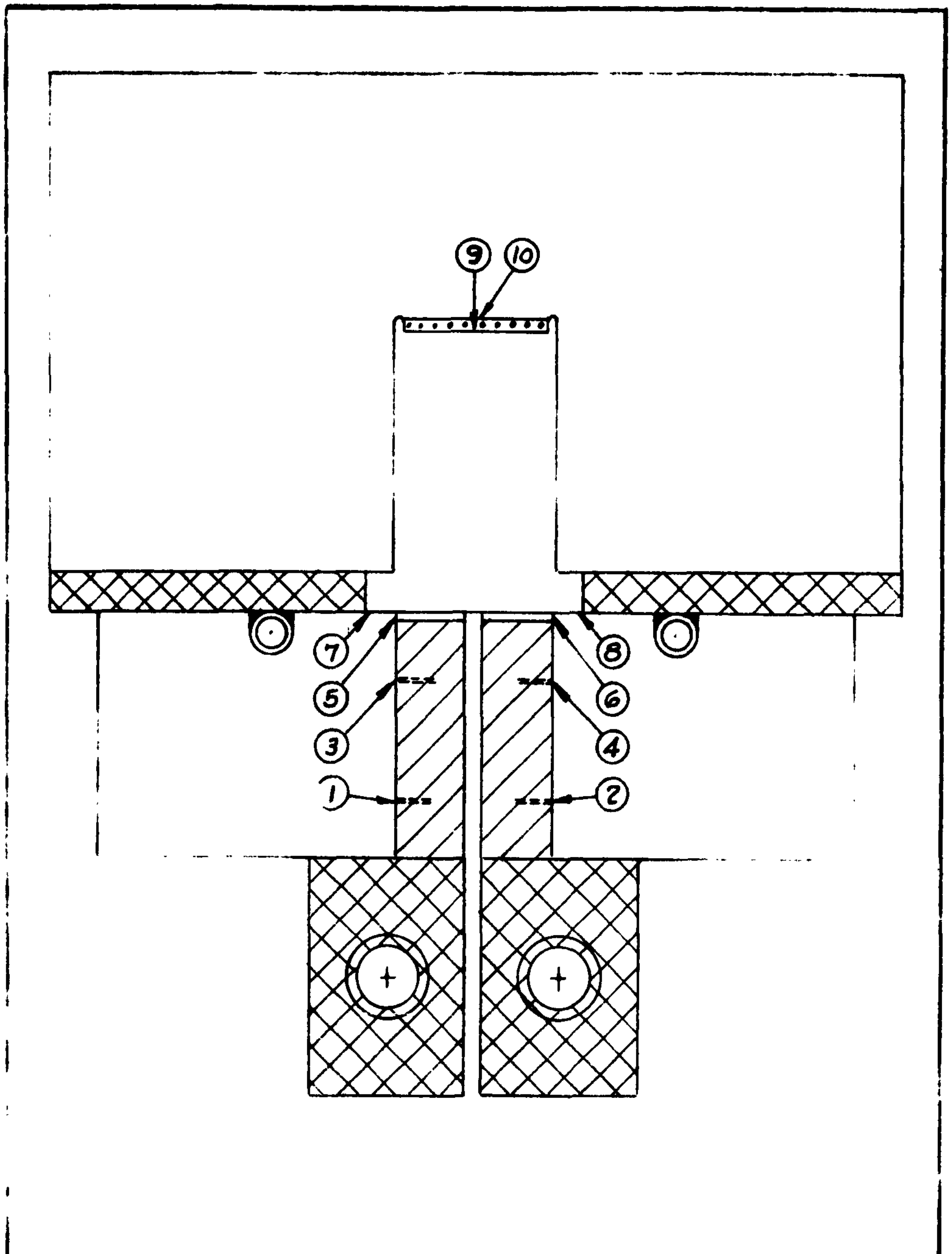
A sketch of the test set-up is shown in Figure 4. Numbered points indicate thermocouple positions.

* Phone conversation D. Gibson to J.H. Bredt.

The heat source consisted of about seven spiral-wound turns of 0.20 inch nichrome wire which fit neatly into the cylindrical recess on the hot end of the cartridge. This was embedded in a pool of Sauereisen #1 cement in the recess. A thermocouple was spot welded to the cartridge cap in the center. A second thermocouple was sealed to the top of the insulating cement surface to measure the surface temperature of the heater.

To measure the heat flow from the cold end lugs, 3/4 inch long pieces of Armco iron with a cross-section approximating that of the lugs were prepared with 0.010 inch diameter holes, 0.389 inches apart (measured along the axis) on the cylindrical surface to accommodate the thermocouples made from No. 40 copper-constantan wire. These materials and dimensions were expected to provide 100 MV difference in thermocouple voltages per watt of heat conducted in the axial direction. These were soldered to the lugs protruding from the cold end of the cartridge. To the other end of the thermal shunts were soldered small copper blocks with a 1/4 inch diameter copper tube passing through them.

To be able to determine the shunt heat loss with a minimum of heat exchange between the case and lugs or elements, it was considered desirable to maintain the cold end of the case at the same temperature as the lugs.



Thermoelectric Power DECO - G.E. Co. Lynn, Mass.	TE CARTRIDGE TEST FACILITY FIGURE 4	Quarterly Report #3 Contract NObs 86854 R.L. Thompson ATL

To do this, a copper plate, 4 inches by 4 inches by 1/8 inch with a hole in the center to accommodate the lower end of the case, was prepared. The plate was split from one edge to the hold to permit clamping around the case. A cooling tube of 1/8 inch copper was soldered to one surface of the plate. Thermocouples were spot welded to each lug and the bottom edge of the case adjacent to the lug thermocouples.

Thermal insulation above the case heat sink consisted of about 2 inches of fibrous potassium titanate around and above the cartridge case. Below the copper plate and around the thermal shunts poly-urethane foam was used.

Current leads were brought out from the copper heat sinks for each lug. Current was measured by the drop through a $10^{-3}\ \Omega$ shunt with a Rubicon portable potentiometer. Output voltages were measured with a Keithley millivoltmeter at the thermocouples spot welded to the lugs. Input power to the heater was determined by measuring current and voltage on P-3 and Ballantine instruments respectively.

Results

About seventeen sets of data were taken at various values of power input, loading, and temperature. For some parameters, this provided a good basis for averaging of the data.

The main reason for this large number was to get a "feel" for the apparatus and to gradually work up to the maximum operating temperatures. Only the salient features of the data appear in Table I. Some remarks that should be made about some of the data that appear in Table I follow.

Because of the large changes in the hot junction temperature due to electrical loading of the generator, it was necessary to consider the open circuit voltage at the instant after the load is removed rather than the equilibrium open circuit voltage. This was determined by using a time based recorder showing the voltage as a function of time during switching operation from the load to no-load condition.

TABLE I

Heater input power	23.5 watts
Case temperature in center of cap	748°C
Heat rejected from N lug	7.35 watts
Heat rejected from P lug	7.83 watts
Total heat rejected from lugs	15.18 watts
% of input power rejected by lugs*	61%
Open circuit voltage	.254 volts
Closed circuit voltage	.127 volts
Closed circuit current	5.19 amps
Calculated resistance (lug to lug)	.024 ohms
Power delivered to load	.654 watts
Over-all efficiency	2.56%
Net efficiency	4.14%
Estimated cold junction temperature	86°C
Estimated hot junction temperature	590°C
Thermal resistance from hot cap to hot junction*	10°C/watt
Lug to case thermal resistance	10°C/watt

* Average values based upon several measurements.

The over-all efficiency is based upon the input power to the heat source and includes shunt heat losses as well as others such as thermal insulation losses. The net efficiency is based upon the heat extracted from the lugs plus that appearing at the load.

The cold junction temperature is based upon a calculated thermal resistance in the lugs of 1.7°C/watt.

The hot junction temperature is determined by the measured open circuit voltage and the 3M curves of Seebeck voltage as a function of temperature with correction for the cold junction temperature.

The lug to the case thermal resistance was calculated in one instance. When the case was cooled 20°F below the temperature of the lugs, the shunt heat loss was about two watts higher than normal.

SECTION II - OPTIMIZED CARTRIDGE

II-1 Definition

A study has been completed to determine the optimized "cartridge couple" configuration. Ambiguity surrounding the use of the term "optimized" necessitates a definition from the onset. Our objectives in arriving at the optimized design are given below.

(1) Increase specific power/weight.
(2) Decrease shunt heat loss.
(3) Decrease temperature gradients at the hot and cold ends.
(4) Decrease junction electrical resistance.
(5) Simplify assembly techniques.
(6) Lower manufacturing costs.

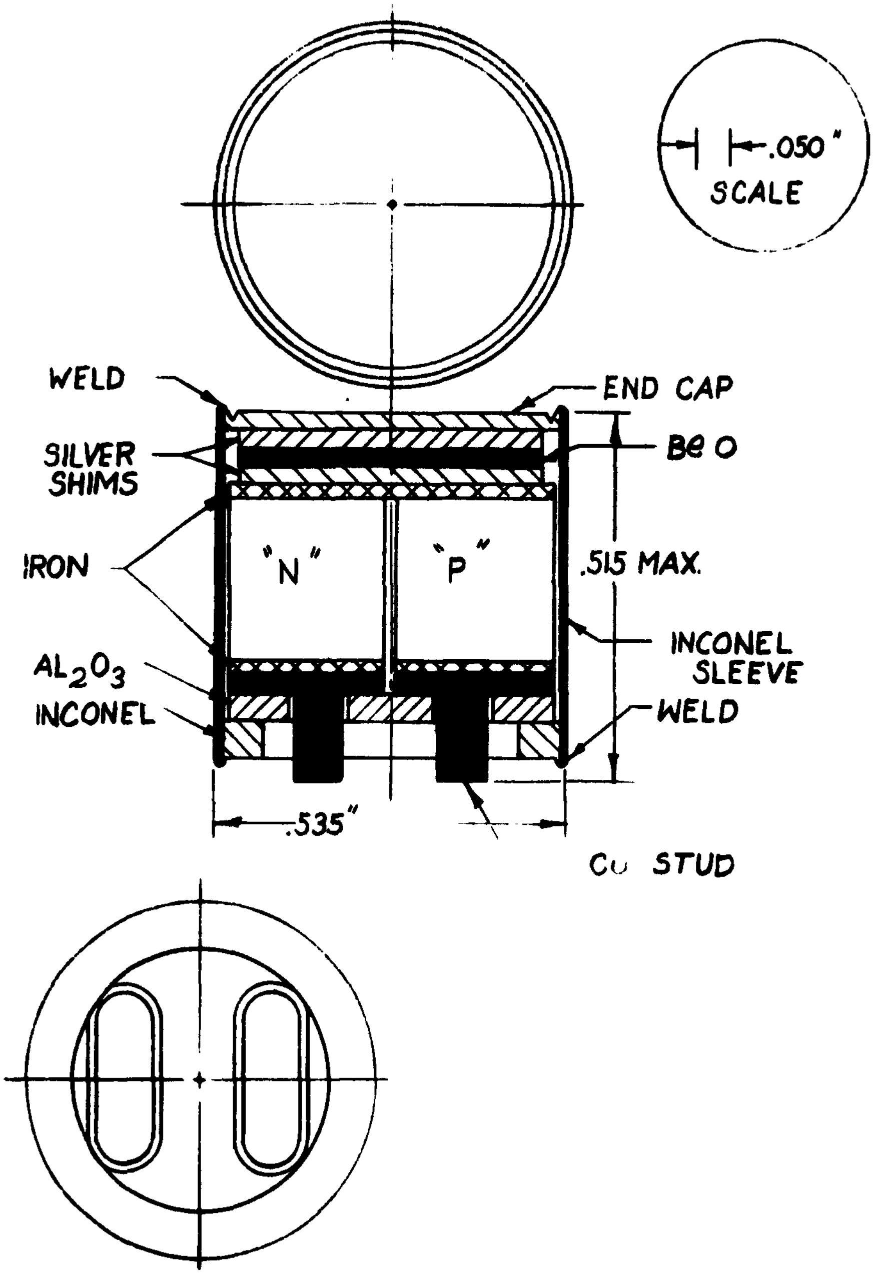
Test data obtained to date clearly demonstrates the soundness of the cartridge approach. However, certain areas requiring improvement have been recognized and experience obtained from the prototype design has been utilized in the redesigned cartridge. Each cartridge placed on test reflected changes deemed necessary from an evaluation of its predecessor. For example, electrical loading at the hot junction during operation was corrected by increasing the thickness of the bridge material. Corrosion was observed at the cold end soldered joint and extreme care was taken in succeeding circuits to neutralize the flux.

II-2 Weight and Structural Integrity

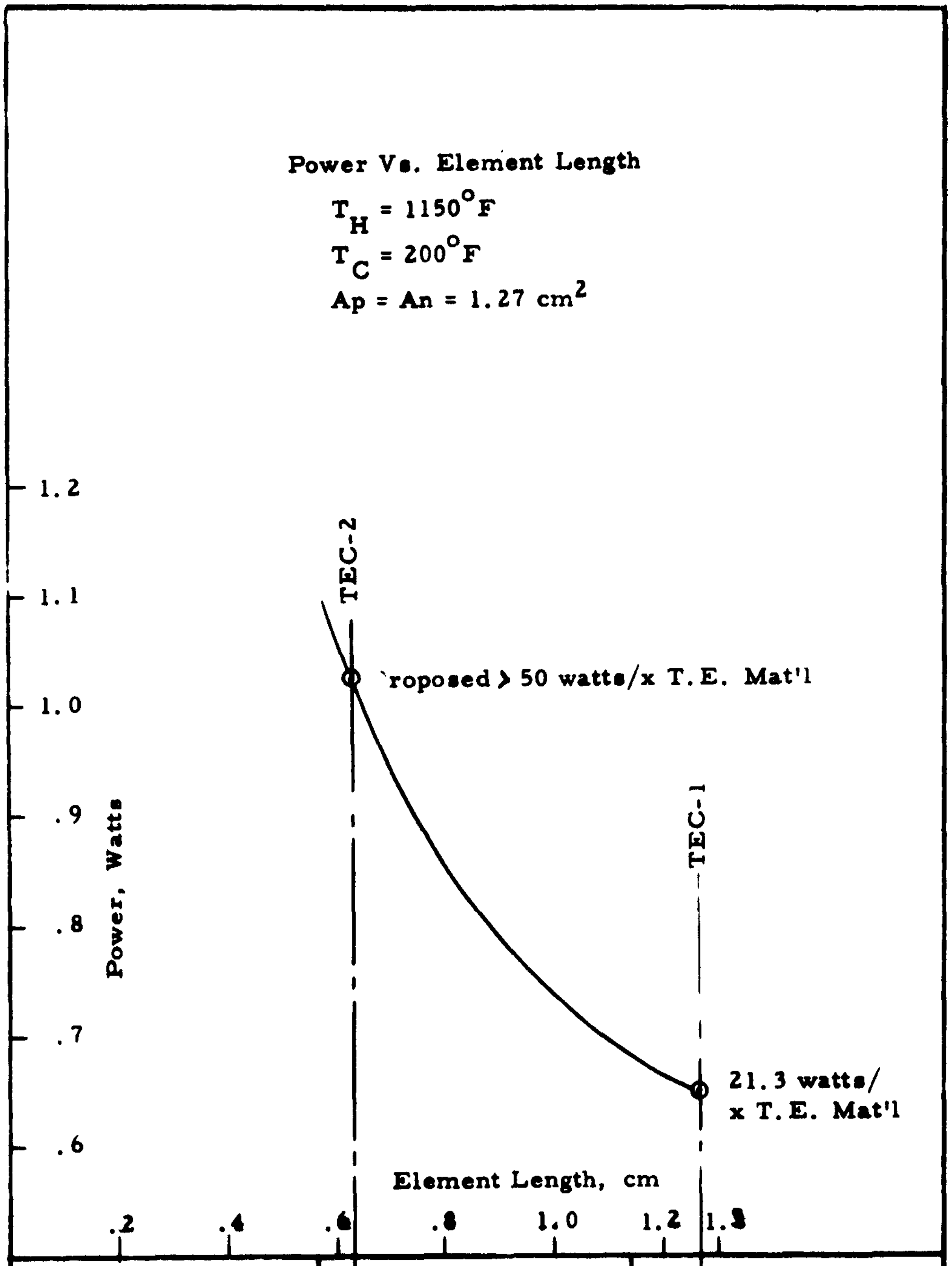
The optimized cartridge couple is shown in Figure 5. In order to reduce weight, the radius has been removed from the base. Instead the sleeve is straight with welds at either end. Elimination of the radius results in a more rigid design with improved structural integrity. This change was considered necessary since a two mil sleeve thickness is required to hold shunt heat loss to a tolerable level (approximately 13%).

II-3 Lead Telluride Elements

The lead telluride elements have been reduced from the original length of 1.27 cm to 0.6 cm. This change will be reflected in increased power to 1.1 watts per couple providing junction resistance remains unchanged. See Figure 6. Couple efficiency will be approximately 4.3% with an r/ρ ratio (junction resistance/element resistance) of 0.75 cm. Theoretical power for a couple with negligible junction resistance is 2.2 watts with an attendant increase in efficiency. This clearly indicates the necessity for reducing junction resistance to the minimal value.



Thermoelectric Power DECO - G. E. Co. Lynn, Mass.	REDESIGNED CARTRIDGE ASSEMBLY DWG. FIGURE 5	Quarterly Report #3 Contract NObs 86854 D. J. Gibson



Thermoelectric Power DECO - G. E. Co. Lynn, Mass.	FIGURE 6	Quarterly Report #3 Contract NObs 86854 D. J. Gibson

II-4 Iron to Lead Telluride Bonds

The original couple design called for a single bonded iron bridge to cover both "P" and "N" elements. Repeated attempts to obtain this bridge were unsuccessful since the "P" element cracked and lowered itself from the bridge material. The approach, therefore, was to individually bond iron to cylindrical "P" or "N" elements and then section each along its axis. The junction was then formed by pressure loading a silver bridge to contact iron on the elements.

Techniques for improving the iron-lead telluride bond are currently being investigated and are listed below. It is believed that one of these techniques will permit bridging electrically with a single iron end cap.

Exploratory Bonding Techniques:

(1) Hot pressed iron (current practice).
(2) Tin telluride bonds.
(3) Gas pressure bonding.

(1) Hot pressed iron end caps provide fairly low electrical resistance but result in cracks in the "P" element. Cartridge testing did not result in separation of iron from lead telluride elements at the hot end when subjected to temperature cycling. However, at the cold end, separation of iron from elements was observed in several of the test specimens.

This is caused by the presence of residual flux in the interface and is extremely difficult, if not impossible, to remove. Methods of eliminating the flux problem are described later in the report.

(2) Tin telluride bonds are currently being explored as a solution to a number of problems coincident with the hot pressed technique. It is believed that iron will be bonded to lead telluride without cracking the elements since extremely low pressure is used.

A 100 gram quantity of tin telluride has been purchased from Tyco Laboratories, Waltham, Mass. Tyco researchers claim that joint strength is higher than that of PbTe itself. They also state that the SnTe braze matches the Fe well and that the SnTe - PbTe solid solution (formed during the brazing cycle) provides a graded type of bond. Again, their data on thermal cycling is incomplete. Most thermocouples that Tyco has bonded to date have been sent to Diamond Ordnance Fuze Laboratories for evaluation and results have not yet been received. Plans to work closely with Tyco Laboratories in an evaluation of SnTe bonds used within the cartridge assembly have been completed.

The use of SnTe would permit brazing iron with electro-plated copper to PbTe elements. This, in turn, eliminates the cold side flux problem since the tinned iron is believed easily soldered to copper electrodes without the use of flux. If flux is required, rosin may be used and the excess easily removed.

(3) A program has been established with Battelle Memorial Institute, Columbus, Ohio, for the gas pressure bonding of iron to PbTe elements. Attempts will be made to form diffusion bonds between iron and PbTe by enclosing the material in a close fitting metallic enclosure and applying uniform pressure on the assembly during the bonding operation. Our objective here is to obtain a single iron bridge across the hot end PbTe elements.

Although limited life testing to 2000 hours seems to indicate that the differential expansion technique used to load the junction bridge is successful, long period operation could result in a loss of contact pressure. Either creep in the Inconel sleeve or plastic flow within the internal composite assembly could result in this undesirable effect. If this results, an alternate design employing a braided wire bridge with surface brazed to adjacent parts may provide the required flexibility without dependence on differential expansion.

II-5 Hot End Electrical Insulation

Measurements of temperature on the cap and TE elements show a ΔT of 150°F in a compression assembly. The hot cap temperature must, therefore, be 1300°F to produce a junction temperature of 1150°F. The relatively high cap temperatures places severe demands upon the burner and its structure. A study has, therefore, been conducted to diminish the hot end temperature gradient through a complete brazed assembly to iron end caps with BeO substituted for the Al_2O_3 insulating wafer. At a temperature level of 1200°F the thermal conductivity of BeO is greater than that of Al_2O_3 by at least a factor of four. Since BeO will be purchased in ready-to-use form and sealed within the cartridge, no toxicity problems are anticipated. In order to avoid the toxicity problem attendant with the use of beryllia, cartridges will not be disassembled for inspection. Of course, in the field, cartridges will not be disassembled for any reason since grinding or sawing into the BeO could produce a dust, toxic through inhalation or entry through a body opening.

Our analysis shows that a hot side ΔT of 50°F or less is possible with these improvements to the design.

II-6 Silver Buffers

Silver buffers will be retained in the hot side assembly. The reasons for this are two-fold: (1) Attempts to braze low expansion rate metallic oxide ceramics to adjacent metallic members produces cracks in the ceramic unless a silver interface is employed; (2) The silver has been seen to flow plastically in the hot end assembly and thus provides better seating of materials due to non uniform loading, while eliminating to some extent the propagation of cracks in PbTe elements.

II-7 Base Seal Assembly

An Al_2O_3 insulator has been substituted for the pressed mica to provide improved strength for the base seal assembly. In addition, alumina provides an improved heat conducting path to the base terminals thereby diminishing the temperature at the cold junctions. It must also be recognized that the shunt heat loss through alumina will be greater in the vicinity of the base, but sleeve thickness has been reduced to limit shunt loss. It is believed that the gain in the substitution of Al_2O_3 more than offsets the improved thermally conducting path for shunt heat in the vicinity of the base.

II-8 Electrical Terminals

Copper end terminals have been substituted for the original stainless steel to improve the heat conducting paths and consequently lowering the temperature gradient to the cold junctions. Accompanying the thermal improvement there is also a small, but not insignificant, improvement in electrical conductivity. As mentioned earlier, soldering to copper is easily accomplished and should eliminate flux problems encountered in the original design.

II-9 Conclusions

It is indicated that information obtained from the prototype unit has been properly employed in the redesigned cartridge. Results from the original design are gratifying, considering problems that are normally attendant with new product development. The success in problem isolation and solution has resulted in numerous changes in the original conceptual design, which are also reflected in the redesigned unit.

Considerable effort has been directed toward lowering hot side junction resistance since the greatest advances lie in this area. Isostatic bonding as well as brazing with tin telluride shall be explored through the cartridge couple assembly technique.

It is believed that the redesigned unit meets the definition of the optimized configuration. Only through test can these improvements be measured and evaluated. Ten redesigned cartridges shall be fabricated and tested for power, efficiency, and life insofar as time permits.

Included with this report are assembly and detail drawings of the redesigned cartridge (Figures 7 through 14). It should be noted that a significant weight and volume reduction has been effected. Total cartridge weight has been reduced to 65% of the original and through the use of a sleeve thickness of less than 1 mil, shunt heat has diminished to one-half of the prototype measured value.

II-10 Thermoelectric Generator Systems Study

Information shown in Table II has been provided by J.H. Bredt, General Engineering Laboratory, General Electric Company, to show performance obtained with the incorporation of the "cartridge couple" into a generator assembly. It will be noted that burner efficiency and fan power deduction are included in the tabulated data. No attempt has been made to optimize the generator, but performance is considered typical.

Data given in columns (1) and (2) are for an idealized system which includes insulation but does not consider shunt heat loss through the container walls and structural supports. Columns identified by (12W) and (22W) pertain to the cartridge couple assembly with 0.002 inch wall thickness.

Of particular interest is the efficiency and power/weight obtained in each case. It appears that 50 watts/pound is possible with generator efficiency greater than 2.5%.

TABLE II

COMPARISON OF SYSTEMS WITH AND WITHOUT 2 MIL METAL ENCAPSULATING TUBES

System	1	2	12W	22W
Ambient air temp: °F	120	120	120	120
r/ρ ratio: cm	.75	.75	.75	.75
Gross watts per lb. of PbTe	50	50	50	50
Watts per ft^2 of fin base	250	160	218	140
Watts fan power per ft^2 of fin base area	8	5.1	8	5.1
Ft^2 fin base area per kw net output	4.13	6.45	4.75	7.41
Watts fan power per kw net output	33	33	38	38
$G = \frac{\text{fin base area}}{\text{thermoelement area}}$	1.87	3.12	2.14	3.58
Lb. of thermal insulation per kw net output	.70	1.74	.93	2.14
Lb. of heat exchanger and thermal insulation per kw net output	20	20	20	20
Lb. of heat exchanger per ft^2 of fin base area	4.67	2.83	4.01	2.41
Fin base temperature: °C	158	142	162	146
Cold junction temp: °C	188	162	192	166
Thermoelement length: cm	.56	.61	.55	.60
Energy conversion efficiency	4.33%	4.70%	4.27%	4.64%
Module efficiency	4.24%	4.61%	3.68%	3.99%
Module efficiency after fan power deduction	4.10%	4.46%	3.55%	3.84%
Overall efficiency				
with 65% efficient burner	2.67%	2.90%	2.31%	2.50%
with 75% efficient burner	3.08%	3.34%	2.66%	2.88%
Lb. fuel burner per net kw hr				
with 65% efficient burner	6.73	6.20	7.78	7.19
with 75% efficient burner	5.83	5.38	6.75	6.24
Net kw hr from 5 gals. gasoline				
with 65% efficient burner	4.57	4.96	3.96	4.28
with 75% efficient burner	5.28	5.72	4.55	4.93

TABLE II (Cont'd)

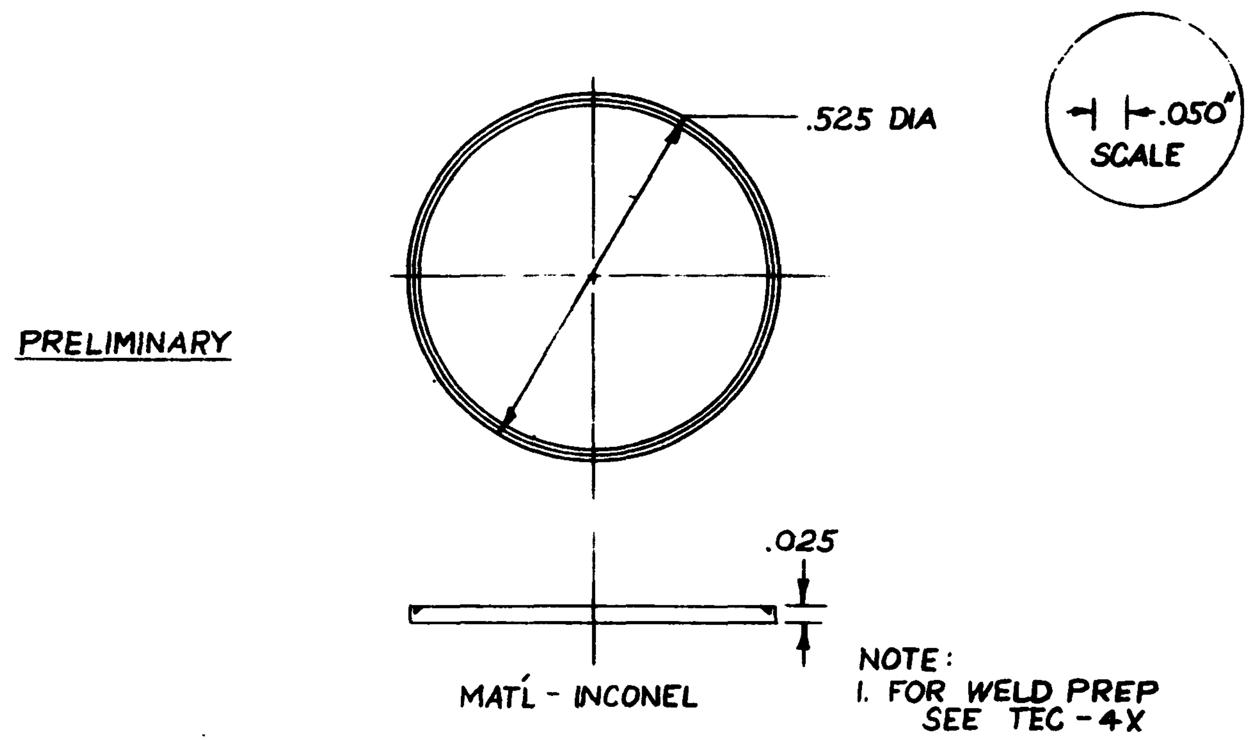
COMPARISON OF SYSTEMS WITH AND WITHOUT 2 MIL METAL ENCAPSULATING TUBES

	1	2	12W	22W
Fin length: in.	1.5	1.5	1.5	1.5
Fin height: in.	3.75	3.75	3.75	3.75
Length of fin base: ft per net kw output	13.2	20.6	15.2	23.7
Area of fin system per net kw normal to air flow: ft^2	1.65	2.58	1.90	2.96
Volume of heat exchanger and modules per net kw output: ft^3	.61	.96	.70	1.11
Net kw output per ft^3 of heat exchanger and modules	1.64	1.04	1.43	.90

Redesigned Cartridge

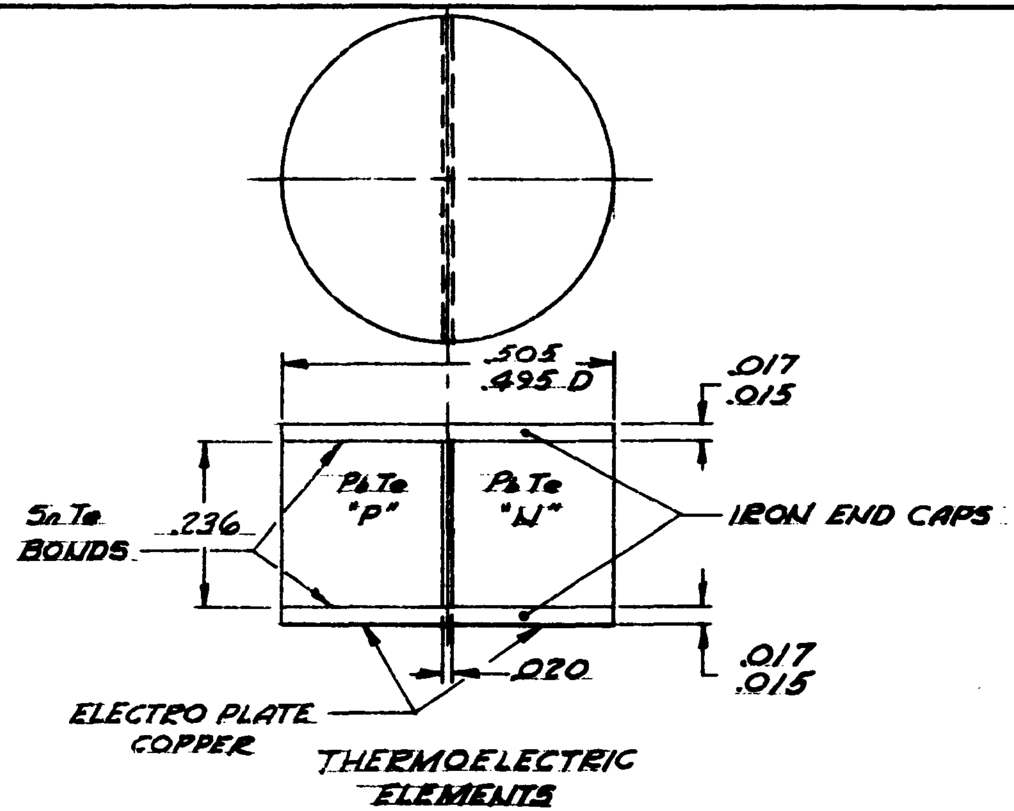
Assembly and Detail Drawings

Figure 7 - Figure 14

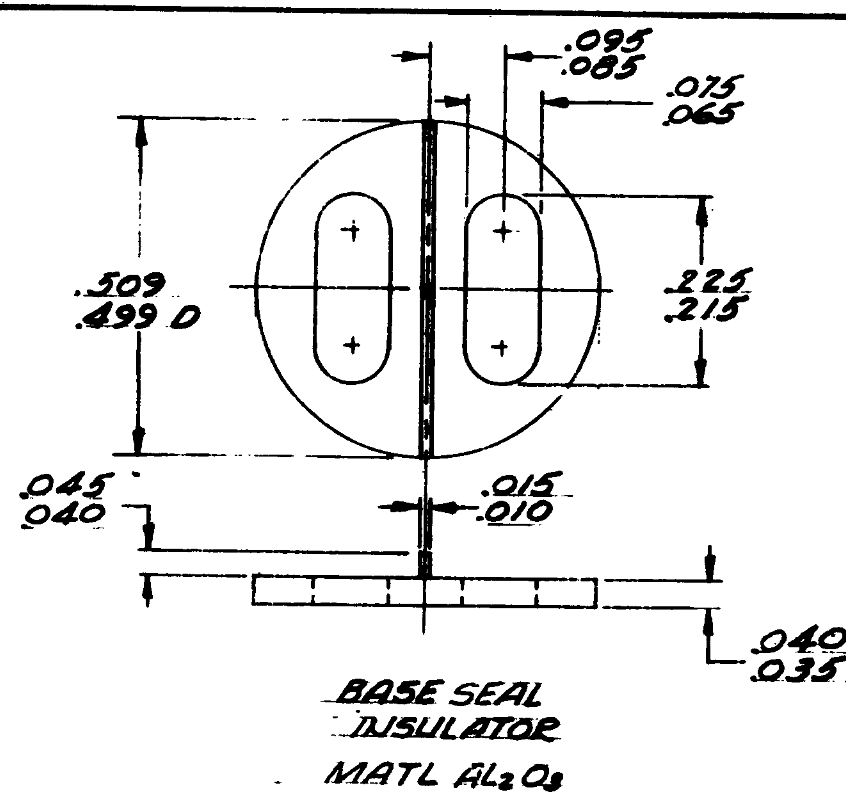


CAP

Thermoelectric Power DECO - G.E. Co. Lynn, Mass.	TEC-1X FIGURE 7	Quarterly Report #3 Contract NObs 86854 D. J. Gibson



Thermoelectric Power DECO - G.E. Co. Lynn, Mass.	TEC-2X FIGURE 8	Quarterly Report #3 Contract NObs 86854 D.J. Gibson

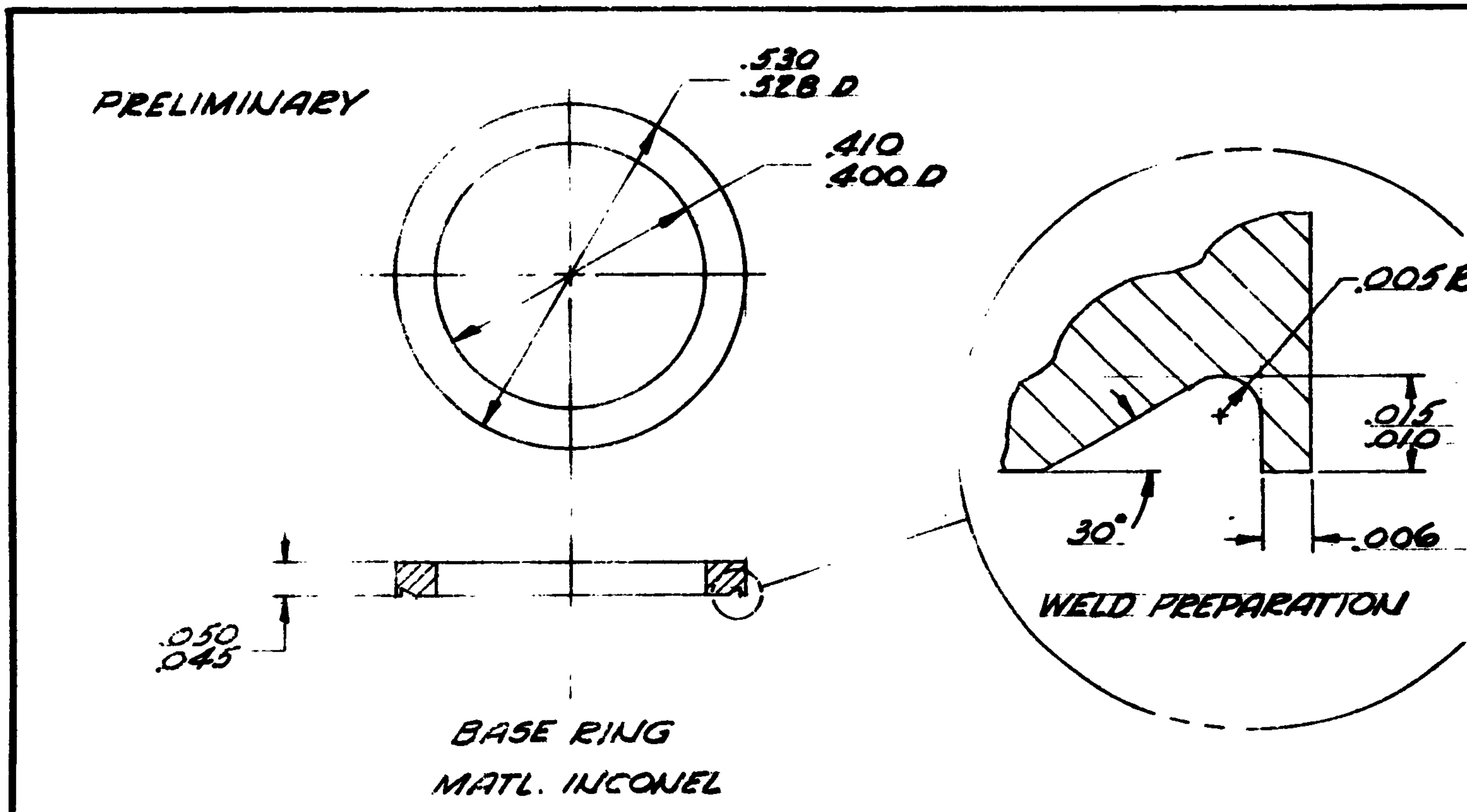


Thermoelectric Power
DECO - G.E. Co.
Lynn, Mass.

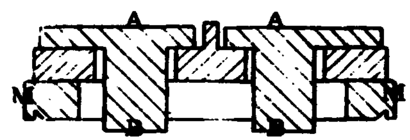
TEC-3X

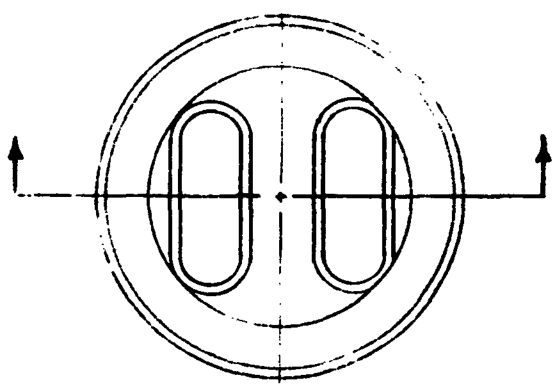
FIGURE 9

Quarterly Report #3
Contract NObs 86854
D. J. Gibson



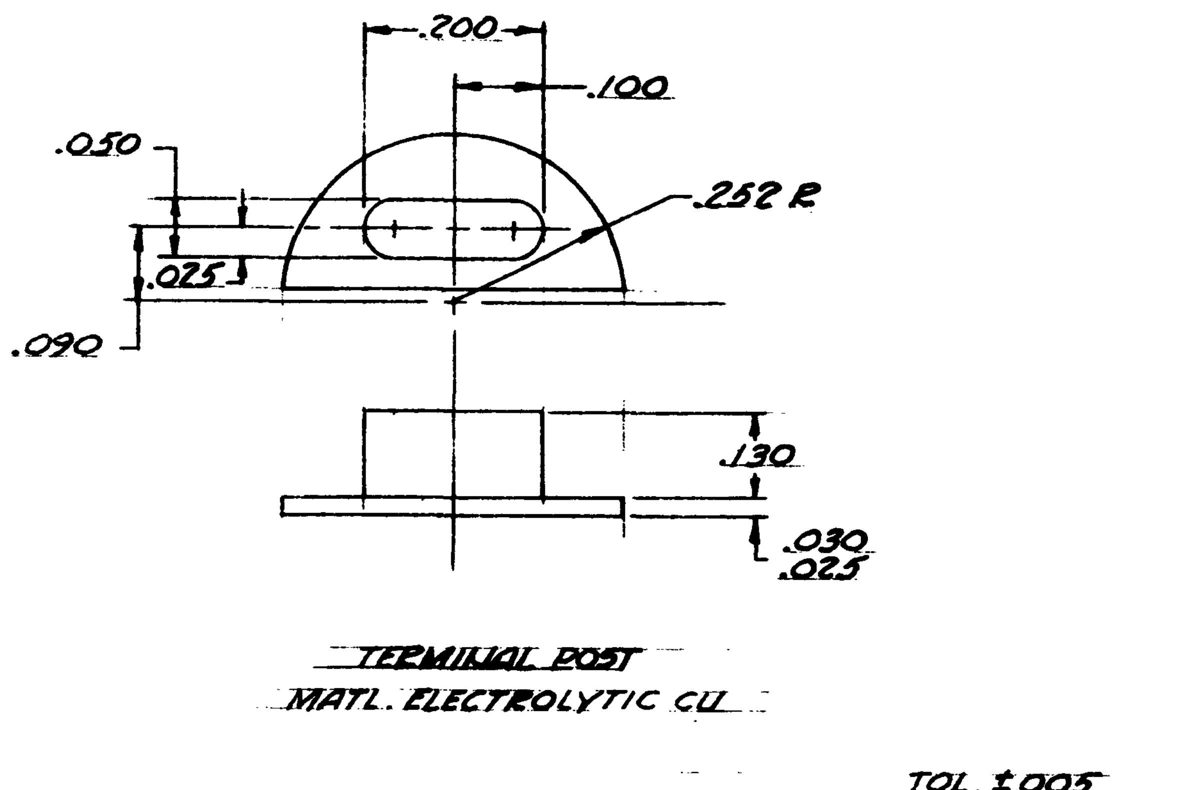
Thermoelectric Power DECO - G.E. Co. Lynn, Mass.	TEC-4X FIGURE 10	Quarterly Report #3 Contract NObs 86854 D. J. Gibson



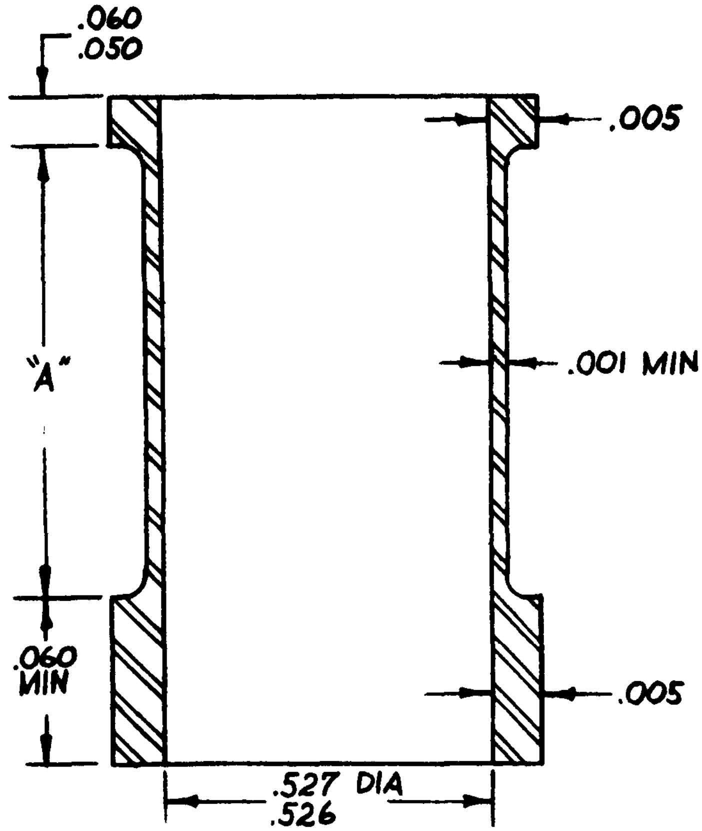


Surfaces A-A & B-B to be parallel within .002 T.I.R. & ⊥ to M-M within .002 T.I.R

Thermoelectric Power DECO - G.E. Co Lynn, Mass.	ASSEMBLY OF TEC PARTS 3X, 4X, 5X FIGURE 11	Quarterly Report #3 Contract NObs 86854 D.J. Gibson



Thermoelectric Power DECO - G.E. Co. Lynn, Mass.	TEC-5X FIGURE 12	Quarterly Report #3 Contract NObs 86854 D. J. Gibson

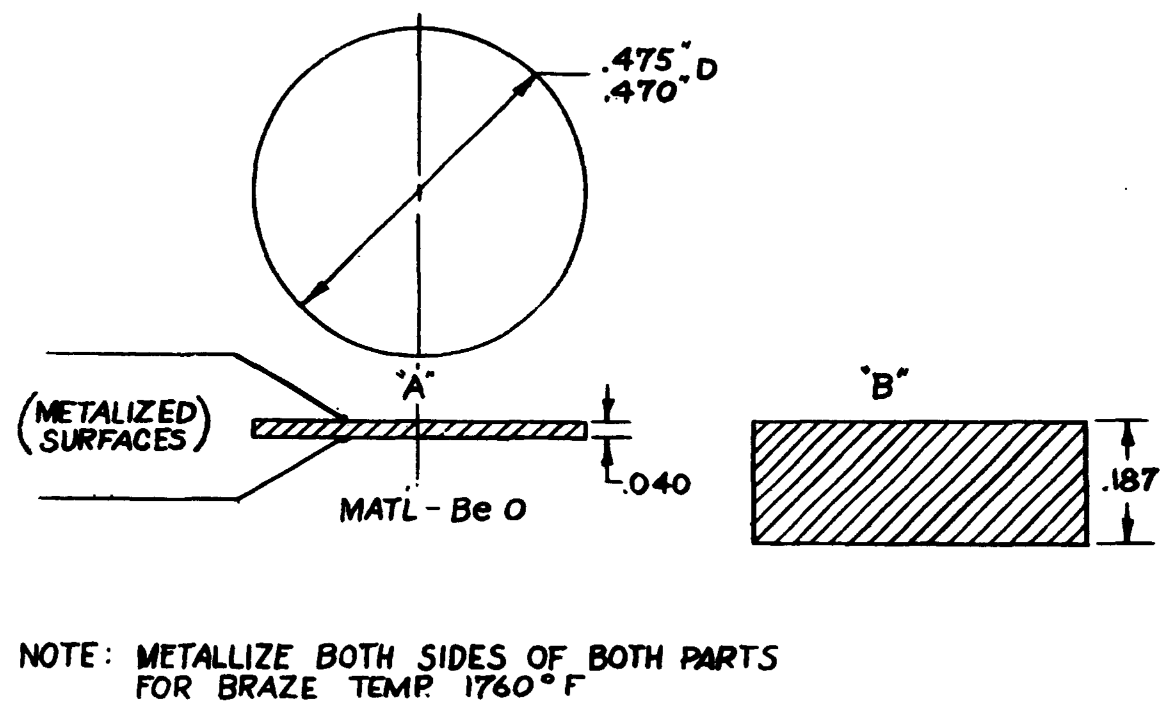


PART	DIM "A"
1	.321 -.351
2	.492 -.522

SCALE : NONE

SLEEVE

Thermoelectric Power DECO - G.E. Co. Lynn, Mass.	TEC-6X FIGURE 13	Quarterly Report #3 Contract NObs 86854 D. J. Gibson



INSULATOR

Thermoelectric Power DECO - G.E. Co. Lynn, Mass.	TEC-7X FIGURE 14	Quarterly Report #3 Contract NObs 86854 D. J. Gibson